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(54) **Wet laid fibrous thermoplastic material and aqueous dispersion for producing same**
Nassgelegtes faseriges thermoplastisches Material und wässrige Dispersion zu dessen Herstellung
Matériau fibreux thermoplastique formé humide et dispersion aqueuse pour sa préparation

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EP-A- 0 511 235 GB-A- 2 046 324
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Description

The present invention relates to a process for manufacturing a fiber-containing material with thermoplastic polymer that can be molded, and also relates to the material so manufactured. More particularly, the present invention relates to a process for manufacturing a material having a thermoplastic polymer matrix and chopped chemically treated glass fibers, where both the fibers and thermoplastic polymer is prepared into moldable material by a wet-laid process, and also relates to the material particularly so manufactured.

Fiber reinforced plastics include thermoplastic moldable materials and thermosetting moldable materials. The latter includes sheet molding compounds, thick molding compounds and the like that mold through curing. The fiber reinforced thermoplastics mold through flowing the material into a shape as in an injection, compression molding operations. In compression molding a fiber reinforced thermoplastic composite is placed in a mold and stamped to the desired shape. These materials for such an operation are produced in the form of laminates containing the fibers in various forms including chopped strand continuous strand mats and needled mats and mixtures thereof and the thermoplastic polymer matrix combined with the reinforcement through lamination, extrudication processes. Also, processes have been developed recently where the reinforcement is combined with the thermoplastic polymer in a wet laid process from an aqueous solution containing the fibrous reinforcement in chopped form and the thermoplastic polymer. In this process, the composite ingredients are combined and mixed in water at low solids concentration and equipment similar to a hydropulper used in the formation of paper from paper pulp. After the slurry is properly mixed, it can be pumped as a thick stock to a holding device where the slurry is further diluted and flocculated and pumped to a head box of a paper machine. Also the slurry can be pumped directed to the head box of the paper machine.

From the head box, the composite sheet is formed on a continuous traveling wire mesh. The mesh takes the composite over vacuum sources to remove liquids including water and form the sheet. A mat binder usually polyvinylpyrrolidone is sprayed onto the sheet and the sheet is dried. Representative of such processes are those described in U.S. Patents 4,882,114; 3,716,449, 3,871,952, EP Patent Nos. 0 312 414 and 0 308 286 and 0 341 977.

It is an object of the present invention to provide a process for manufacturing a wet laid fiber-containing thermoplastic composite or material that has good tensile and flexible properties in the molded article, and to provide a material so manufactured.

SUMMARY OF THE INVENTION

In accordance with the present invention the aforementioned and other objects gleaned from the disclosure herein are achieved by a process of forming a wet-laid, nonwoven, glass fiber containing thermoplastic polymer web that is moldable as a fiber reinforced thermoplastic laminate. The process comprises

(A) forming an aqueous dispersion containing:

- (1) a thermoplastic matrix polymer in particulate powder form, said thermoplastic matrix polymer being selected from the group consisting of polyolefins, polyesters, polyamides, polyphenylene oxide and polycarbonates and being used in such an amount that it constitutes at least 50 weight percent of the wet-laid web to be formed;
- (2) discontinuous glass fibers treated with a forming size containing (a) at least one watersoluble, film forming polymer or copolymer, (b) an organo coupling agent selected from the group consisting of an organo functional alkoxysilane essentially devoid of primary mono-amine functionality, an ureido-modified amino silane, and a vinyl organo functional silane, and (c) a cationic lubricant, wherein the forming size aids the glass fibers in dispersing them in the aqueous dispersion, the glass fibers being used in such an amount that they constitute from 1 to 50 weight percent of the wet-laid web to be formed;

(B) removing water from the aqueous dispersion of step (A) to form a wet-laid, sheet-like mat; and

(C) applying to the wet-laid, sheet-like mat of step (B) a mat binder having a solids content from 0.1 to 32 weight percent and comprising

- (1) a chemically modified thermoplastic polymer selected from carboxylic modified polyolefins;
- (2) a film forming polymer selected from the group consisting of epoxy polymers, polyurethane polymers, epoxy polyurethane copolymers, polyvinylpyrrolidone and polyoxyalkylene;

the mat binder being applied in such an amount that the chemically modified thermoplastic polymer contained therein constitutes 0.01 to 20 weight of the wet-laid web; and

(D) drying the mat binder treated wet-laid, sheet-like mat of step (C) to form the wet-laid, non-woven, fiber containing web.

The wet-laid web includes: the nonwoven mat of discontinuous glass fibers, thermoplastic matrix polymer, and chemically modified thermoplastic polymer having chemically reactive moieties for addition, condensation or free radical reaction to allow for coupling of the glass fiber to the matrix polymer. The glass fibers have a surface treatment or "size" that allows the fibers to disperse even from the strand form in an aqueous dispersion that does or is to contain the thermoplastic matrix polymer. Dispersion of the fibers can be assisted by surfactants in the size or in the aqueous dispersion. The aqueous dispersion of the glass fibers and thermoplastic matrix polymer can be any white water dispersion or foam dispersion for the wet-laid process of forming a web. The chemically modified thermoplastic polymer can be added as a powder or as pellets to the aqueous dispersion or as an emulsion or dispersion in a mat binder that is applied to the wet laid web of fibers and polymer. The foam aqueous dispersion has sufficient surfactants to assure formation of the foam dispersion. The dried laminate is formed by drying the web that has a reduced moisture content at a temperature elevated from ambient temperatures. The thermoplastic laminate is moldable into shaped articles.

DETAILED DESCRIPTION OF THE INVENTION

In the specification and in the claims, the below-defined terms have the following meanings.

The "white water system" is an aqueous solution in which the glass fibers are dispersed and which can contain numerous dispersants, thickeners, softening, hardening chemicals, or dispersed or emulsified thermoplastic polymers. Examples of various white water systems include aqueous solutions having polyacrylamide polymers such as the Separan polymer available from Dow Chemical Company, alone or with hydroxyethyl cellulose and the like suspending aids to provide a highly viscous aqueous solution at high material concentrations. Also, white water systems include those having any of the numerous amine oxide surfactants as shown in U.S. Patent 4,179,331. An example of the polyacrylamides are those shown in U.S. Patent 4,395,306. In addition to such chemicals as polyacrylamides or amine oxides being present in the white water system, there can also be present small amounts of surfactants such as polyethoxylated derivatives of amide condensation products of fatty acids and polyethylene polyamines as is shown in U.S. Patent 4,265,704. Also numerous other chemical agents can be added to a white water system as is known by those skilled in the art.

The wet-laid process of producing a fiber-containing thermoplastic web involves forming an aqueous dispersion of discontinuous fibers like chopped fibers or chopped strands and the thermoplastic polymer usually with agitation in a mixing tank. The aqueous dispersion, usually referred to as slush or pulping medium, is processed into the wet-laid, sheet-like mat by such machines as cylinder or Fourdrinier machines or more technologically advanced machinery, such as the Stevens Former, RotoFormer, Inver Former and the VertiFormer machines. The slush is deposited from a head box onto a moving wire screen or onto the surface of a moving wire-covered cylinder. The slurry on the screen or cylinder is processed into the nonwoven, sheet-like mat by the removal of water, usually by a suction and/or vacuum device, and by the application of a mat binder. Water and excess binder are removed by suction and/or vacuum devices. The web of binder treated nonwoven, sheet-like glass fiber mat and thermoplastic matrix polymer is dried in one or more ovens. The wet-laid process also includes the use of an aqueous foam as the aqueous dispersion to produce the slush rather than a traditional white water. The foam contains the thermoplastic polymer in addition to the glass fibers, along with one or more surfactants and water. This process is more fully discussed in U.S. Patents 4,882,114; 4,690,860; and British patent documents 1,129,757 and 1,329,409.

Formation of the aqueous dispersion of the fibers and thermoplastic matrix polymer in accordance with these processes, it is achieved merely by placing the chopped glass fibers whether wet or dried of the desired length into a batch of water with or without the addition of dispersing agents and before or after the addition of the thermoplastic matrix polymer usually with agitation and/or turbulence. A foamed aqueous dispersion is obtained by adding one or more surfactants.

Generally, the foamed aqueous dispersion is prepared with from 20 to 60 percent by weight of single discrete glass fibers having a high modulus amine elasticity and from 40 to 80 percent by weight of the thermoplastic matrix polymer where the matrix polymer has a particle size of less than 1.5mm. From this foamed aqueous dispersion in a wet-laid process, a web is formed by laying down the dispersion on a mesh to allow for removal of excess water and application of any mat binder. The web is then transferred to a heating oven. The heating removes residual moisture from the web and also bonds the fibrous and plastic components together into a self-sustained permeable sheet.

In the wet-laid process, the fibers that are used are glass fibers. Generally, the amount of the discontinuous fibers in the aqueous dispersion can range from 0.001 to 5 and preferably 0.01 to 3 weight percent of the aqueous dispersion. Placement of the fibers into the dispersion occurs with or without the use of dispersing agents. In any event, the glass fibers have a treatment with a forming size that aids in dispersing them in the aqueous dispersion. Suitable examples of chopped glass fibers that can be used are those having a surface treatment having at least one water-soluble, film-forming polymer or copolymer that has an intrinsic viscosity of less than 500 mPa.s (centipoise), a matrix resin compatible organo functional alkoxy silane, wherein the organic moieties is essentially devoid of primary mono-amine functionality and the alkoxy group can range from 1 to 3 and can be hydrolyzed or unhydrolyzed. Also the surface

treatment in the undried aqueous form has a water-soluble, dispersible and/or emulsifiable cationic lubricant and optionally one or more cationic epichlorohydrin polyamine adducts. Generally, the film-forming copolymer is present in an effective film-forming amount; there again the functional silane is present in an amount from 0.4 to 20, the cationic lubricant is present in an amount to 0.1 to 15 and the cationic amine polymer epichlorohydrin is present in an amount from 0.4 to an amount that is not detrimental to the dispersibility of the treated fibers in water. Particularly suitable treated glass fibers are those having a surface treatment having on a weight percent solids basis 70 to 80 weight percent of poly(vinylalcohol), 5 to 10 weight percent cationic lubricant, 5 to 10 weight percent ureido-modified amino silane, and 1 to 10 weight percent epichlorohydrin available from Georgia Pacific as GP2925 material. Another suitable example are glass fibers having a surface treatment of a crosslinkable polyurethane film-forming polymer, at least one organo functional silane coupling agent, a copolymer of at least one polymerizable acrylic-type, at least one monomer that is addition polymerizable and matrix-resin miscible and matrix-resin reactable. An example of such a surface treatment is one having the poly(vinyl alcohol) polymer in an amount of 85 to 95 weight percent of the solids, an amount of a cationic lubricant in an amount of around 0.1 to 1 weight percent of the solids and epichlorohydrin-polyamide adduct like Polycup® 172 in an amount of around 3 to 10 weight percent and a vinyl organo functional silane like A-151 from Union Carbide Corporation in an amount from 1 to 8 weight percent and an amount of acetic acid for hydrolyzing the silane. Typically, the amount of surface treatment present on the fibers is in the range from 0.15 to 0.45 weight percent of the strands.

The thermoplastic matrix polymer useful in forming the aqueous dispersion and web material is in a particulate form or pelletized form which is then ground into a particular powder form. Suitable materials include polyethylene, polypropylene, polyethylene terephthalate, polybutylene terephthalate and plasticized versions thereof. Additional suitable examples of the thermoplastic matrix polymer include polyesters, polyamides, polyphenylene oxide, and polycarbonate.

The mat binder, which is applied to the wet-laid, sheet like mat obtained in step (A) of the above process of the invention, comprises (1) a thermoplastic carboxylic modified polyolefin and (2) a film forming polymer. Generally, the particle size of the chemically modified thermoplastic is similar to that of the thermoplastic matrix polymer. A non-exclusive example of a suitable particle size is that in the range of 100 to 1100 μm (microns). The chemically modified thermoplastic polymer is one having the chemically reactive moieties and being carboxylic acid and/or carboxylic anhydride modified polyolefins such as maleic anhydride modified polypropylene and maleic acid modified polypropylene and mixtures and blends of these. These types of materials are more fully discussed in U.S. Patent Nos. 3,416,990 (Robinson) and 3,437,550 (Paul) and 3,483,276 (Mahlman). Generally, the acid modification involves modifying the polyolefins with carboxylic and/or polycarboxylic acids and/or anhydrides.

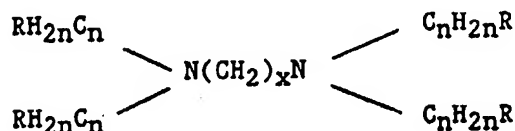
The chemically modified thermoplastic in addition to combination with components to form the aqueous mat binder dispersion can be added to the web as the mat binder or along with traditional mat binders. A suitable binder would be that described in U.S. Patent 4,728,573. Generally, the mat binders have one or more amine organo coupling agents, an aqueous emulsion dispersion of carboxylic-modified polyolefin resin that has been neutralized or nearly neutralized with an organic or inorganic base with an aqueous soluble dispersible or emulsifiable film-forming polymer and with or without a binder stabilizer. The basicity of the organic or inorganic base used to neutralize the carboxylic containing polyolefin polymer is less than the basicity or (Kb) or any amino group of the coupling agent. For instance, the acid modified polyolefin can be neutralized with a base having a pKb or basicity similar to that of diethyl ethanolamine. Such a mat binder material would have present on a weight percent solids basis up to 100 percent of the solids of the chemically modified thermoplastic polymer, from 0 to 50 percent weight solids of the organic coupling agent capable of donating electrons and from 0 to 25 weight percent of the solids of the mono-, poly-, aliphatic or cyclic carboxylic acid and/or anhydride and from 0 to 30 weight percent of a film-forming polymer. Useful film-forming polymers include epoxy polymers from epoxy emulsions, polyurethane polymers from polyurethane emulsions and epoxy polyurethane copolymers from such emulsions and polyvinyl pyrrolidone and mixtures and blends of these.

Another suitable example of a mat binder includes a thermoplastic or thermosetting film forming polymer such as: a polyurethane, including polyester urethane and polyether urethane and polyurea-urethane, polyoxyalkylene like poly(oxyethylene-oxypropylene) copolymers and thermoplastic polymers. The polymeric composition also has effective stabilizing amounts of stabilizing agents selected from: metal deactivating agents such as polydentate ligands like ethylenediaminetetraacetic acid (EDTA), low temperature anti-oxidant, and higher temperature anti-oxidant. Additionally, a crosslinking agent may be present.

A suitable example is a mat binder having:

- a. at least one matrix-compatible film-forming polymer in an effective film-forming amount,
- b. at least one organofunctional silane coupling agent selected from the group consisting of aminoalkyl alkoxysilanes, polyaminoalkyl alkoxysilanes in an effective coupling agent amount,
- c. at least two stabilizing agents selected from:

i. a metal deactivating agent selected from polydentate ligands and those having the following formula:



ii. lower temperature anti-oxidant selected from: hydrosulfite, bisulfite, phosphorous acid, phosphite and phosphite-containing reducing agent selected from the group consisting of alkali metal hypophosphites, alkaline earth metal hypophosphites, hydrogen phosphites and ammonium hypophosphite in an effective antioxidant amount,

iii. higher temperature anti-oxidant selected from alkali metal phenyl phosphinates and alkaline earth metal phenyl phosphonates, and phenyl-containing thioethers and polymers thereof, thiodipropionate like di(tridecyl) thiodipropionate and mixtures thereof in an effective anti-oxidant amount.

One particular formulation of such a binder is:

	Solids %
Oil-in-water emulsion of the curable matrix-compatible polyurethane film forming polymer	40-70
Water for polymer emulsion	
A-1100® gamma-aminopropyltriethoxy silane	62
Water for A-1100	
Hampene® NA2 disodium ethylene diamine tetraacetate	100
Sodium Hypophosphite	100
Water for Hampene and Hypophosphite	
RD-1135B epoxidized polyester	20
Evanstab® 13 (Di(Tridecyl)thiodipropionate	100
Baybond® XW-116 (blocked aliphatic polyisocyanate crosslinker)	70
Hot water for Baybond	
Rhoplex® E-693 acrylic copolymer	50
Water for Rhoplex	

Water for dilution to 100 gallons

% Solids:	9.0 ± 0.3
pH in Pa.s	10 ± 0.5
Viscosity: °C(cp)*	3 ± 1 (3 ± 1)
Temperature (°F)	27 ± 6 (80 ± 10)

*cp = centipoise

The binder can be formulated by adding the polymer latices to premix tanks with slow stirring and the addition of about 1/5 of the total volume of water as deionized water. In this formulation an acrylic copolymer latex is used which assists in producing improved solvent resistance for reinforcing polyamide. The Rhoplex® E-693 material is available from Rohm and Haas Co., Philadelphia, Pennsylvania. This material is a white emulsion having a solids content of 49.5 to 50.5 percent with a pH of 4.5 to 6.5 and a viscosity at LVT (1), 60 rpm 20-60. This copolymer is a self-crosslinking acrylic-type copolymer of the anionic emulsifying type with a density at 20°C of 1.05 g/cm³ (8.8 pounds per gallon) and minimum film-forming temperature of ±12°C and a temperature at which the torsional modulus of an air dried film is 300 kilograms per centimeter² of +24°C. About 2/5 of the total volume of water is added to a main mix tank and the amino organofunctional silane is added to this deionized water with slow stirring. The polymer latex premixes are added to the silane mixture in the main mix and stirred for five minutes and added to the main mix tank. The polyisocyanate crosslinking agent is added to a premix tank and has added to it hot water with stirring. After the emulsion forms, it is stirred for five minutes and then added to the main mix tank. The acrylic copolymer is added to a premix tank with a small amount of water, around 1/30 of the total volume of water needed for the chemical treating composition and the mixture is stirred for five minutes and added to the main mix tank. The aqueous chemical treating composition is diluted with deionized water to its final desired volume.

The aforementioned various mat binders are formulated to have a solids content in the range of 0.1 to 32 weight percent and preferably 5 to 18 weight percent. The mat binders are applied to the web of nonwoven fibers and thermoplastic matrix polymer without any method known to those skilled in the art for applying mat binders. This is referred to applying the binder by spraying the web after most of the water from the slush has been removed on the mesh or screen of the wet-laid process.

The amounts of the glass fiber thermoplastic matrix polymer and chemically modified thermoplastic polymer present in the web produced by the wet-laid process can be in the following ranges. The nonwoven mat can range from 1 to 50 weight percent of the web; the thermoplastic matrix polymer constitutes more than 50 weight percent of the web; and the chemically modified thermoplastic polymer can range from 0.01 to 20 weight percent of the wet-laid web. Generally, the amount of chemically modified thermoplastic polymer present in the web varies to a degree with the amount of chemical modification of the thermoplastic polymer. Suitable examples of materials that can be added directly to the slush include the Hercoprime material available from Himont and the Excelor material available from Exxon Chemical Company. The latter material is used in an amount greater than the former since the former appears to have a greater degree of functionality. The amount for the former preferably ranges from 0.1 to 5 weight percent of the web and the amount for the latter can range from 0.1 to 16 weight percent of the web.

With formation of the web having the chemically modified thermoplastic polymer, the web is dried to further reduce the moisture and to initiate some degree of reaction between the chemically modified thermoplastic polymer and the fibers. Typically, the drying occurs in an oven at an elevated temperature above ambient and generally in a temperature above the melting point of the thermoplastic matrix polymer. For example, when the thermoplastic polymer is a polypropylene the drying temperature can be by hot air and 100 to 240°C, preferably 120°C to 180°C. A suitable oven is a drying oven manufactured by Honeycomb Engineering Company.

The various aspects of the invention will be illustrated in the following examples.

Example 1

In the preferred embodiment of the present invention, a wet-laid nonwoven web with thermoplastic polymer having a grammage equal to 1000 grams per meter² and the components of Table 1 below was formed. The manner of forming the web was that similar to the methods described in U.S. Patent 4,882,114.

Table 1

Fina 3860 Homopolymer of Polypropylene	66 percent
Melt Flow Index = 75 grams/10 minutes	
Irgafos® 168 Phosphite Antioxidant	3 percent
Naugard® 445 Aromatic Amine Anti-oxidant	1 percent
1.3 cm (1/2 inch) glass fiber strands	30 percent

The weight percent of Table 1 is that of the formulation composition. The glass fibers in the strands had a diameter of 16 µm (microns) and had a chemical treatment at a level of 0.30 percent by weight of the strand, where the treatment was an aqueous chemical composition composed of the following solids:

SIZE TREATMENT		
	I	II
Poly(vinylalcohol) Vinol® 205	77.5	88.6
Cationic lubricant (Cat-X® lubricant)	7.04	0.54
Ureido-modified aminosilane	8.04	--
Vinylorganofunctional silane A151	--	4.21
Epichlorohydrin-polyamide adduct (GP 2935)	7.4	6.68
		(Polycup® 172)

The resultant nonwoven web (Grammage = 1000 g/m²) comprised of 66 percent Fina® 3860, 3 percent Irgafos® 168, 1 percent Naugar® 445 and 30 percent glass fibers I was treated at a level 0.86 percent by weight with an aqueous chemical composition comprised of:

75%	Protolube® 5440 Maleic acid, modified polypropylene emulsion from National Starch
12.8%	A-1100® gamma aminopropyltriethoxysilane from Union Carbide Corporation

(continued)

5,1%	Maleic acid (General Chemical Corp.)
7.2%	Epirez® W60-5520, epoxy polyurethane dispersion available from Rhone-Poulenc
0.1%	Antifoam® 1430 available from Dow Corning Corp.
% based on total dry solids.	

Added to the web in conjunction with the web binder was a carbon black dispersion at a level of 0,1%. The resultant treated web was dried to 0% moisture at a temperature of 149°C (300°F). Four dried sheets were stacked and laminated at 216°C, 172 kPa (420°F, 25 psi) for 3.5 minutes. The resultant laminate was cooled at full pressure for 13 minutes. Said laminate was compression molded by heating it to 238°C (460°F) for 6 minutes then shaping a flat panel at 100 tons pressure. The resultant molded panel was cut and tested in accordance with ASTM Procedures for Tensile, Flex and Izod Impact and the values are shown in the following table. The values stated for strength and modulus are normalized to a 30 percent glass loading by weight. This adjustment is accomplished by first determining the actual glass content via an ashing technique then determine the percentage difference between the nominal and actual volume percent glass and multiplying that percentage difference by the strength or modulus value measured. This procedure is carried out for all strength and modulus values reported since webs might vary in glass content by 1 or 2 percent by weight.

Exp. Results				
	Ten Str. kPa (psi)	Flex Str. kPa (psi)	Flex MOD kPa (psi)	Izod Imp. J/m (Ft-lbs/in)
Composition	85,500 kPa	125,500	5,025,000	412
Formulation:	(12,400)	(18,200)	(728,900)	(7.70)

Examples 2-21 and Illustrative A and B

Twenty-one wet laid webs and two illustrative wet laid webs were prepared from components shown in Table 2. The Illustrative examples are indicated as A-B, where Illustrative Examples A and B were made in a manner similar to Example 1, except that poly(vinylpyrrolidone) was the mat binder. Illustrative example A was prepared in a manner similar to Illustrative Example B but without the presence of carbon black. Examples 2 and 3 were prepared in a manner similar to that of Example 1, but carbon black was not used. Examples 4-7 were prepared in a manner similar to that of Example 1 with one of two mat binders and without carbon black. In addition, examples 4-7 and 8 had an addition of the chemically modified polypropylene to the aqueous slush. Also examples 8-23 were prepared in a manner similar to Example 1 with the presence of carbon black and examples 8-12 varied the type of mat binder. Examples 13-20 were prepared in a manner similar to Example 1 but with the addition of the chemically modified polypropylene either to the slush as Hercoprime® polypropylene or to the mat binder as Protolube® 5440 polypropylene emulsion. In these examples the following components were used:

PVP K-90:	Polyvinyl pyrrolidone, MW = 660,000
Hercoprime® G :	Maleic anhydride, Modified Polypropylene
Hercoprime® HG 201:	Maleic anhydride, Modified Polypropylene
Protolube® 5440:	Maleic acid, Modified Propylene
Profax® 6201:	Homopolymer of Polypropylene Melt Flow Index = 20 grams/10 minutes Weight Average MW = 210,000
Fina® 3860:	Homopolymer of Polypropylene Melt Flow Index = 75 grams/10 minutes
Irgafos® 168:	Phosphite Type: Antioxidant which is Tris(2,4-Di-tert-butylphenyl) Phosphite
Naugard® 445:	Aromatic Amine Type: Antioxidant which is 4,4'Di(2,2-dimethylbenzyl)diphenylamine

Glass fiber sample A 1.3 cm (1/2 inch) length and 16 µm fiber diameter Size Treatment I.

Glass fiber sample B 1.3 cm (1/2 inch) length 16 µm fiber diameter with a surface treatment of Size Treatment II.

In examples 2-4, 6, 8, 14, 16, 18 and 20 the mat binder formulation that was used was that as used in example 1 as did examples 15, 17, 19 and 21 with the addition of more of the Protolube® 440 emulsion. Examples 5, 7, 9, and 11 used the mat binder formulation indicated below as "Formulation I". Examples 10 and 12 used the mat binder formulation indicated below as "Formulation II".

Formulation I**% by Actual Solids**

Rucothane® 20116 Polyurethane	56.65
A-1100®	5.34
EDTA	0.31
RD-1135b	5.34

Evan Stab® 13	3.35
Sodium Hypophosphite	1.68
XW-116 M	8.27
Rhoplex® E-693	19.06

Carbon black: Black pigment.

Formulation II

In the formulation for the mat binder of Example 1 the chemically modified polypropylene was removed and replaced with Rucothane® 2011L polyurethane oil-in-water emulsion and it had the following formulation:

	% by Actual Solids
Rucothane® 2011L	51.5%
A-1110®	24.6%
Maleic acid	9.8%
Epirez® W60-5520	14.0%
Anti-foam® 1430	0.1%

Formulation III

	% by Actual Solids
Protolube® 5440	51.5
A-1100	24.6
Maleic acid	9.8
Epirez® W60-5520	14.0
Antifoam® 1430	0.1

TABLE 2

Ingredients	A	B	2	3	4	5	6	7	8	9	10	11	12
Profax® 6201	66	66	66	-	66	66	-	-	-	-	-	-	-
Fina® 3860	-	-	-	66	-	-	66	66	66	66	66	66	66
Irgafos® 168	3	3	3	3	3	3	3	3	3	3	3	3	3
Naugard® 445	1	1	1	1	1	1	1	1	1	1	1	1	1
Glass fibers II	30	30	-	-	-	-	-	-	-	-	-	-	-
Glass fibers I	-	-	30	30	30	30	30	30	30	30	30	30	30
Formulation I	-	-	-	-	-	0.41	-	0.41	-	0.41	-	0.41	-
Formulation III	-	-	0.41	0.41	0.41	-	0.41	-	0.41	-	-	-	-
PVP K-90	0.41	0.41	-	-	-	-	-	-	-	-	-	-	-
Hercoprime® G	-	-	-	-	-	4.0	4.0	4.0	1.0	1.0	1.0	-	-
Hercoprime® HG201	-	-	-	-	-	-	-	-	-	-	-	-	-
Protolube® 5440	-	-	-	-	-	-	-	-	-	-	-	-	-
Formulation II	-	-	-	-	-	-	-	-	-	-	0.41	-	0.41
Carbon Black	-	0.41	-	-	-	-	-	-	0.41	0.41	0.41	0.41	0.41

TABLE 2 (Cont'd)

Ingredients	13	14	15	16	17	18	19	20	21	22
Fina® 3860	66	66	66	66	66	66	66	66	66	66
Glass fibers I	30	30	30	30	30	30	30	30	30	30
Irgafos® 168	3	3	3	3	3	3	3	3	3	3
Naugard® 445	1	1	1	1	1	1	1	1	1	1
Carbon Black	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21
Formulation III	0.29	0.29	0.62	0.62	0.29	0.29	0.62	0.62	0.29	0.14
Hercoprime® HG201	1.0	-	1.0	-	1.0	-	1.0	-	-	-
Protolube® 5440	-	0.41	-	0.41	-	0.41	-	0.41	-	-

The wet laid nonwoven material with the thermoplastic polymer produced in Table 2 were molded under conditions similar to that of Example 1. The molded samples were tested in a manner similar to those of example 1 for tensile, flexural and impact properties. These test results are presented in Table 3.

TABLE 3
EXPERIMENTAL RESULTS

COMPOSITE FORMULATION	TEN STR. MD/CMD kPa(PSI)	FLEX STR. MD/CMD kPa(PSI)	FLEX MOD. MD/CMD mPa(PSI)	IZOD IMP. MD/CMD J/m(FT-LBS/IN)
1	94,500(13,700)	115,100(16,700)	4,806(697,000)	813(15.2)
	55,800(8,100)	110,300(16,000)	4,212(610,900)	529(9.9)
AVG	75,200(10,900)	113,000(16,400)	4,509(654,000)	674(12.6)
2	109,000(15,800)	126,900(18,400)	4,773(692,300)	856(16.0)
	76,500(11,100)	114,500(16,600)	4,116(597,000)	535(10.0)
AVG	93,000(13,500)	120,700(17,500)	4,445(644,700)	695(13.0)
3	128,000(18,600)	144,100(20,900)	5,626(816,000)	834(15.6)
	82,000(11,900)	119,300(17,300)	4,432(642,800)	508(9.5)
AVG	105,500(15,300)	131,700(19,100)	5,029(729,400)	674(12.6)
4	127,000(18,400)	171,700(24,900)	6,119(887,500)	380(7.1)
	84,100(12,200)	128,900(18,700)	4,502(653,000)	299(5.6)
AVG	105,500(15,300)	150,300(21,800)	5,311(770,300)	342(6.4)
5	117,200(17,000)	152,400(22,100)	5,632(816,800)	369(6.9)
	91,700(13,300)	120,000(17,400)	4,249(616,300)	294(5.5)
AVG	104,800(15,200)	136,500(19,800)	4,940(716,600)	342(6.4)
6	124,100(18,000)	159,800(23,200)	5,619(814,900)	406(7.6)
	76,500(11,100)	117,200(17,000)	4,318(626,300)	294(5.5)
AVG	100,700(14,600)	138,600(20,100)	4,969(720,600)	353(6.6)
7	121,400(17,600)	151,700(22,000)	5,344(775,100)	401(7.5)
	115,100(16,700)	129,000(18,700)	4,524(656,100)	305(5.7)
AVG	118,600(17,200)	140,700(20,400)	4,934(715,600)	332(6.2)
8	95,200(13,800)	133,100(19,300)	5,504(798,200)	364(6.81)
	64,800(9,400)	114,500(16,600)	4,065(589,500)	299(5.60)
AVG	80,000(11,600)	123,400(17,900)	4,784(693,800)	332(6.20)

5	9	89,600(13,000)	126,900(18,400)	5,203(754,600)	310(5.80)
		60,700(8,800)	82,100(11,900)	3,090(448,200)	235(4.40)
	AVG	75,200(10,900)	104,800(15,200)	4,147(601,400)	273(5.10)
10	10	71,000(10,300)	111,700(16,200)	4,947(717,500)	353(6.60)
		59,300(8,600)	97,900(14,200)	3,778(548,000)	278(5.20)
	AVG	65,500(9,500)	104,800(15,200)	6,895(632,700)	315(5.90)
15	11	76,500(11,100)	106,200(15,400)	5,039(730,800)	529(9.90)
		51,000(7,400)	82,100(11,900)	3,472(503,500)	348(6.50)
	AVG	64,100(9,300)	93,800(13,600)	4,256(617,200)	438(8.20)
20	12	69,600(10,100)	127,600(18,500)	5,459(791,700)	492(9.20)
		61,400(8,900)	86,900(12,600)	3,425(496,700)	380(7.10)
	AVG	65,500(9,500)	107,600(15,600)	4,442(644,200)	438(8.20)
25	13	65,500(9,500)	113,100(16,400)	5,682(737,100)	471(9.30)
		49,000(7,100)	93,100(13,500)	3,667(531,800)	364(6.80)
	AVG	57,200(8,300)	103,400(15,000)	4,375(634,500)	417(7.80)
30	1	94,500(13,700)	115,100(16,700)	4,806(697,000)	813(15.20)
		56,000(8,100)	110,300(16,000)	4,212(610,900)	529(9.90)
	AVG	75,200(10,900)	113,100(16,400)	4,509(654,000)	674(12.60)

Adjusted Physical Properties

TRIAL #	TEN STR.	FLEX STR.	FLEX MOD.	IZOD IMP.
	MD/CMD	MD/CMD	MD/CMD	MD/CMD
	kPa(psi)	kPa(psi)	mPa(psi)	J/m(FT-LBS/IN)
14	91,014(13,200)	117,900(17,100)	4,698(681,400)	438(8.20)
	60,000(8,700)	117,200(17,000)	4,815(698,400)	315(5.90)
	AVG 80,700 11,000	117,900(17,100)	4,751(689,000)	380(7.10)
15	104,800(15,200)	143,400(20,300)	5,784(838,900)	540(10.10)
	55,200(8,000)	90,600(13,140)	3,686(534,600)	348(6.50)
	AVG 11,600	117,200(17,000)	4,701(681,800)	444(8.30)
16	80,000(13,000)	130,300(18,900)	5,670(822,300)	438(8.20)
	59,300(8,600)	94,500(13,700)	3,781(548,500)	390(7.30)
	AVG 74,500(10,800)	112,400(16,300)	4,726(685,400)	417(7.80)
17	93,100(13,500)	149,600(21,700)	5,957(863,900)	551(10.30)
	58,600(8,500)	103,400(15,000)	4,393(637,100)	332(6.20)
	AVG 75,800(11,000)	126,900(18,400)	5,175(750,500)	444(8.30)
18	100,000(14,500)	151,000(21,900)	6,188(897,400)	369(6.90)
	71,000(10,300)	126,900(18,400)	4,631(671,600)	310(5.80)
	AVG 85,500(12,400)	139,300(20,200)	5,409(784,500)	342(6.40)

19	97,200(14,100)	177,900(25,800)	6,827(990,100)	396(7.40)
	56,500(8,200)	111,000(16,100)	4,115(596,800)	294(5.50)
AVG	74,200(11,200)	144,800(21,000)	5,469(793,500)	348(6.50)

20	115,100(16,700)	151,700(22,000)	6,139(890,300)	284(5.30)
	51,000(7,400)	91,700(13,300)	3,552(515,200)	273(5.10)
AVG	83,400(12,100)	120,000(17,700)	702,800	278(5.20)

21	107,600(15,600)	156,500(22,700)	4,486(951,400)	471(8.80)
	62,700(9,100)	93,800(13,600)	3,491(506,300)	348(6.50)
AVG	85,500(12,400)	125,500(18,200)	5,026(728,900)	412(7.70)

22	86,900(12,600)	136,500(19,800)	5,976(866,700)	521(9.751)
				412(7.709)
				364(6.808)
	50,300(7,300)	117,900(17,100)	4,453(645,900)	316(5.909)
AVG	69,900(10,000)	127,600(18,500)	5,125(756,300)	406(7.60)

23	99,300(14,400)	125,500(18,200)	5,460(791,900)	536(10.02)
	54,500(7,900)	102,700(14,900)	4,032(584,800)	332(6.20)
AVG	77,200(11,200)	114,500(16,600)	4,747(688,400)	433(8.10)

It can be concluded from the study that composite physical properties improve as the melt flow index of the resin matrix is increased and that strength and modulus properties improve but impact performance decreases with the addition of 4 percent maleic anhydride modified polypropylene. The impact performance is reduced significantly because the low molecular weight additive tends to imbrittle the resin matrix thereby reducing the composites ability to absorb energy during impact. At a 1 percent loading the maleic anhydride modified polypropylene additive offers benefits to all performance criteria. It can also be concluded from the study that chemical formulation III gives the best properties of any chemical formulation studied plus the lower the level of carbon black present the better the overall physical properties performance will be. Finally, it was determined that maleic acid and maleic anhydride modified polypropylene could be used interchangeable as part of the composite formulations.

Claims

1. A process of forming a wet-laid, non-woven, glass fiber containing thermoplastic polymer web that is moldable as a fiber reinforced thermoplastic laminate, comprising:

(A) forming an aqueous dispersion containing:

(1) a thermoplastic matrix polymer in particulate powder form, said thermoplastic matrix polymer being selected from the group consisting of polyolefins, polyesters, polyamides, polyphenylene oxide and polycarbonates and being used in such an amount that it constitutes at least 50 weight percent of the wet-laid web to be formed;

(2) discontinuous glass fibers treated with a forming size containing (a) at least one watersoluble, film forming polymer or copolymer, (b) an organo coupling agent selected from the group consisting of an organo functional alkoxysilane essentially devoid of primary mono-amine functionality, an ureido-modified amino silane, and a vinyl organo functional silane, and (c) a cationic lubricant, wherein the forming size aids the glass fibers in dispersing them in the aqueous dispersion, the glass fibers being used in such an amount that they constitute from 1 to 50 weight percent of the wet-laid web to be formed;

(B) removing water from the aqueous dispersion of step (A) to form a wet-laid, sheet-like mat; and

(C) applying to the wet-laid, sheet-like mat of step (B) a mat binder having a solids content from 0.1 to 32 weight percent and comprising

- (1) a chemically modified thermoplastic polymer selected from carboxylic modified polyolefins;
- (2) a film forming polymer selected from the group consisting of epoxy polymers, polyurethane polymers, epoxy polyurethane copolymers, polyvinylpyrrolidone and polyoxyalkylene;

the mat binder being applied in such an amount that the chemically modified thermoplastic polymer contained therein constitutes 0.01 to 20 weight percent of the wet-laid web; and

(D) drying the mat binder treated wet-laid, sheet-like mat of step (C) to form the wet-laid, non-woven, fiber containing web.

2. The process of Claim 1, wherein the aqueous dispersion of step (A) contains one or more surfactants to produce a foam aqueous dispersion.
3. The process of Claims 1 or 2, wherein at least one antioxidant is included.
4. The process of Claim 3, wherein the antioxidant is selected from the group consisting of thioester type antioxidants, phosphite type antioxidants, aromatic amine type antioxidants and combinations thereof.
5. The process of any of Claims 1 to 4, wherein the thermoplastic matrix polymer is polypropylene.
6. The process of any of Claims 1 to 5, wherein the water-soluble, film-forming polymer or copolymer (a) contained in the glass fiber forming size has an intrinsic viscosity of less than 150 centipoise, a molecular weight of from 22,000 to greater than 105,000 and is a polymer of the group consisting of (i) poly(vinylacetate) hydrolyzed at least to a sufficient degree to be water-soluble, (ii) poly(vinylpyrrolidone), (iii) poly(hydroxyalkylcellulose), and (iv) copolymers of monomers for preparing the polymers (i) and (ii), the polymer being present in an amount of up to 98 weight percent of the solids of the forming size.
7. The process of any of Claims 1 to 6, wherein the organo-functional alkoxysilane essentially devoid of primary mono-amine functionality, which is a species of the organo coupling agent (b) contained in the glass fiber forming size, is a hydrolyzed, partially hydrolyzed or unhydrolyzed ureido organo-functional trialkoxy silane, wherein the said trialkoxy silane in all of its forms is present in an amount in the range of from 0.4 to 20 weight percent of the solids of the forming size.
8. The process of any of Claims 1 to 6, wherein the organo-functional alkoxysilane essentially devoid of primary mono-amine functionality, which is a species of the organo coupling agent (b) contained in the glass fiber forming size is a hydrolyzed, partially hydrolyzed or unhydrolyzed vinyl organo-functional trialkoxy silane, wherein the said trialkoxy silane in all of its forms is present in an amount of from 0.4 to 20 weight percent of the forming size.
9. The process of any of Claims 1 to 8, wherein the cationic lubricant (c) contained in the glass fiber forming size comprises is present in an amount in the range of from 0.1 to 15 weight percent of the forming size.
10. The process of any of Claims 1 to 9, wherein the forming size of the glass fibers is present in an amount in the range of from 0.15 to 0.45 weight percent of the glass fibers.
11. The process of any of Claims 1 to 10, wherein the mat binder applied in step (C) comprises a chemically modified thermoplastic polymer (1) which is neutralized or nearly neutralized with an organic or inorganic base.
12. The process of any of Claims 1 to 11, wherein the mat binder applied in step (C) comprises the chemically modified thermoplastic polymer (1) of the mat binder as an aqueous dispersion or emulsion.
13. The process of any of Claims 1 to 12, wherein the mat binder applied in step (C) comprises a chemically modified thermoplastic polymer (1) selected from the group consisting of maleic anhydride modified polypropylene, maleic acid modified polypropylene and mixtures and blends thereof.
14. The process of any of Claims 1 to 13, wherein the mat binder applied in step (C) additionally comprises one or more aminoorgano coupling agents having a primary amine with a basicity greater than that of diethyl ethanolamine.
15. The process of Claim 14, wherein the aminoorgano coupling agent is an aminoorgano-functional silane selected from the group consisting of aminoalkyl alkoxysilanes and polyaminoalkyl alkoxysilanes.

16. The process of any of Claims 1 to 15, wherein the mat binder applied in step (C) additionally comprises an aliphatic or cyclic mono or polycarboxylic acid and/or anhydride.
17. The process of any of Claims 1 to 16, wherein the mat binder applied in step (C) additionally comprises a stabilizing agent selected from metal deactivating agents, low temperature antioxidants and higher temperature antioxidants.

Patentansprüche

1. Verfahren zur Herstellung einer naßgelegten, nicht gewebten, Glasfasern enthaltenden thermoplastischen Polymerbahn, die als faserverstärktes thermoplastisches Laminat formbar ist, wobei man:

(A) eine wäßrige Dispersion herstellt, welche enthält

(1) ein thermoplastisches Matrixpolymer in Form eines teilchenförmigen Pulvers, wobei das thermoplastische Matrixpolymer ausgewählt ist aus der Gruppe, die aus Polyolefinen, Polyestern, Polyamiden, Polyphenylenoxid und Polycarbonaten besteht und in einer solchen Menge verwendet wird, daß es mindestens 50 Gewichtsprozent der herzustellenden naßgelegten Bahn darstellt;

(2) diskontinuierliche Glasfasern, die mit einem Schlichtemittel behandelt wurden, welches enthält (a) mindestens ein wasserlösliches, filmbildendes Polymer oder Copolymer, (b) ein organisches Kupplungsmittel, das ausgewählt ist aus der Gruppe, die aus von primärer Monoaminofunktionalität im wesentlichen freien Organo-funktionalen Alkoxysilanen, Ureido-modifizierten Aminosilanen und Vinylorgano-funktionalen Silanen besteht, und (c) ein kationisches Schmiermittel, wobei das Schlichtemittel für das Dispergieren der Glasfasern in der wäßrigen Dispersion hilfreich ist und wobei die Glasfasern in einer solchen Menge verwendet werden, daß sie 1 bis 50 Gewichtsprozent der herzustellenden naßgelegten Bahn darstellen;

(B) aus der Dispersion der Stufe (A) Wasser entfernt, um eine naßgelegte, flächige Matte zu erzeugen; und
(C) auf die naßgelegte, flächige Matte der Stufe (B) einen Mattenbinder aufbringt, der einen Feststoffgehalt von 0,1 bis 32 Gewichtsprozent hat und enthält

(1) ein chemisch modifiziertes thermoplastisches Polymer, das aus Polyolefinen ausgewählt ist, die Carbonsäure-modifiziert sind;

(2) ein filmbildendes Polymer, das ausgewählt ist aus der Gruppe, die aus Epoxypolymeren, Polyurethanpolymeren, Epoxy-Polyurethan-Copolymeren, Polyvinylpyrrolidon und Polyoxyalkylen besteht;

wobei der Mattenbinder in einer solchen Menge aufgebracht wird, daß das darin enthaltene chemisch modifizierte thermoplastische Polymer 0,01 bis 20 Gewichtsprozent der naßgelegten Bahn darstellt; und

(D) die mit dem Mattenbinder behandelte naßgelegte, flächige Matte der Stufe (C) trocknet, um die naßgelegte, nichtgewebte, Fasern enthaltende Bahn herzustellen.

2. Verfahren nach Anspruch 1, wobei die wäßrige Dispersion der Stufe (A) einen oder mehrere oberflächenaktive Stoffe enthält, um eine geschäumte wäßrige Dispersion herzustellen.

3. Verfahren nach Anspruch 1 oder 2, wobei mindestens ein Antioxidans eingeschlossen ist.

4. Verfahren nach Anspruch 3, wobei das Antioxidans ausgewählt ist aus der Gruppe, die aus Antioxidantien vom Thioester-Typ, Antioxidantien vom Phosphit-Typ, Antioxidantien vom Typ der aromatischen Amine und aus Kombinationen dieser Antioxidantien besteht.

5. Verfahren nach einem der Ansprüche 1 bis 4, wobei das thermoplastische Matrixpolymer Polypropylen ist.

6. Verfahren nach einem der Ansprüche 1 bis 5, wobei das in dem Schlichtemittel für die Glasfasern enthaltene wasserlösliche, filmbildende Polymer oder Copolymer (a) eine intrinsische Viskosität von weniger als 150 Centipoise, ein Molekulargewicht von 22.000 bis mehr als 105.000 hat und ein Polymer aus der Gruppe ist, die aus (i) Poly(vinylacetat), das mindestens bis zu einem solchen Grade hydrolysiert ist, daß es wasserlöslich ist, (ii) Poly(vinylpyrrolidon), (iii) Poly(hydroxyalkylzellulose) und (iv) Copolymeren aus Monomeren für die Herstellung der Polymeren (i) und (ii) besteht, wobei das Polymer in einer Menge von bis zu 98 Gewichtsprozent der Feststoffe des Schlichtemittels vorhanden ist.

7. Verfahren nach einem der Ansprüche 1 bis 6, wobei das von primärer Monoamino-Funktionalität im wesentlichen freie Organo-funktionale Alkoxysilan, das ein Vertreter der in dem Schlichtemittel für die Glasfasern enthaltenen organischen Kupplungsmittel (b) ist, ein hydrolysiertes, teilhydrolysiertes oder nicht hydrolysiertes Ureidoorgano-funktionales Trialkoxysilan ist, wobei das Trialkoxysilan in all seinen Formen in einer Menge im Bereich von 0,4 bis 20 Gewichtsprozent der Feststoffe des Schlichtemittels vorhanden ist.
8. Verfahren nach einem der Ansprüche 1 bis 6, wobei das von primärer Monoamino-Funktionalität im wesentlichen freie Organo-funktionale Alkoxysilan, das ein Vertreter der in dem Schlichtemittel für die Glasfasern enthaltenen organischen Kupplungsmittel (b) ist, ein hydrolysiertes, teilhydrolysiertes oder nicht hydrolysiertes Vinylorgano-funktionales Trialkoxysilan ist, wobei das Trialkoxysilan in all seinen Formen in einer Menge im Bereich von 0,4 bis 20 Gewichtsprozent des Schlichtemittels vorhanden ist.
9. Verfahren nach einem der Ansprüche 1 bis 8, wobei das in dem Schlichtemittel für die Glasfasern enthaltene kationische Schmiermittel (c) in einer Menge im Bereich von 0,1 bis 15 Gewichtsprozent des Schlichtemittels vorhanden ist.
10. Verfahren nach einem der Ansprüche 1 bis 9, wobei das Schlichtemittel für die Glasfasern in einer Menge im Bereich von 0,15 bis 0,45 Gewichtsprozent der Glasfasern vorhanden ist.
11. Verfahren nach einem der Ansprüche 1 bis 10, wobei der in der Stufe (C) aufgebrachte Mattenbinder ein chemisch modifiziertes thermoplastisches Polymer (1) umfaßt, das mit einer organischen oder anorganischen Base neutralisiert oder annähernd neutralisiert ist.
12. Verfahren nach einem der Ansprüche 1 bis 11, wobei der in Stufe (C) aufgebrachte Mattenbinder das chemisch modifizierte thermoplastische Polymer (1) des Mattenbinders als wäßrige Dispersion oder Emulsion enthält.
13. Verfahren nach einem der Ansprüche 1 bis 12, wobei der in Stufe (C) aufgebrachte Mattenbinder ein chemisch modifiziertes thermoplastisches Polymer (1) enthält, das ausgewählt ist aus der Gruppe, die aus Maleinsäureanhydridmodifiziertem Polypropylen, Maleinsäure-modifiziertem Polypropylen und deren Mischungen und Gemischen besteht.
14. Verfahren nach einem der Ansprüche 1 bis 13, wobei der in der Stufe (C) aufgebrachte Mattenbinder zusätzlich ein oder mehrere Amino-organische Kupplungsmittel mit einer primären Aminogruppe mit einer Basizität enthält, die größer ist als die von Diethylethanolamin.
15. Verfahren nach Anspruch 14, wobei das Amino-organische Kupplungsmittel ein Aminoorgano-funktionales Silan ist, das ausgewählt ist aus der Gruppe, die aus Aminoalkylalkoxysilanen und Polyaminoalkylalkoxysilanen besteht.
16. Verfahren nach einem der Ansprüche 1 bis 15, wobei der in der Stufe (C) aufgebrachte Mattenbinder zusätzlich eine aliphatische oder cyclische Mono- oder Polycarbonsäure und/oder ein Anhydrid einer solchen Carbonsäure enthält.
17. Verfahren nach einem der Ansprüche 1 bis 16, wobei der in der Stufe (C) aufgebrachte Mattenbinder zusätzlich ein Stabilisierungsmittel enthält, das ausgewählt ist aus Metalldeaktivierungsmitteln, Antioxidantien für niedrige Temperaturen und Antioxidantien für höhere Temperaturen.

Revendications

1. Procédé de formation d'une nappe ou bande de polymère thermoplastique déposée à l'état humide, non tissée, contenant des fibres de verre, que l'on peut mouler en un stratifié ou lamifié thermoplastique renforcé de fibres, caractérisé en ce que :

(A) on forme une dispersion aqueuse contenant :

(1) un polymère constituant la matrice thermoplastique sous forme de poudre particulaire, ledit polymère formant la matrice thermoplastique étant choisi dans le groupe constitué des polyoléfines, des polyesters, des polyamides, du poly(oxyde de phénylène) et des polycarbonates et s'utilisant en une proportion telle

qu'il constitue au moins 50% en poids de la nappe ou bande déposée à l'état humide à former;
 (2) des fibres de verre discontinues traitées par un ensimage formateur contenant (a) au moins un copolymère ou polymère filmogène soluble dans l'eau, (b) un agent de couplage organique choisi dans le groupe constitué d'un organoalcoxysilane fonctionnel, essentiellement dépourvu d'une fonctionnalité monoamine primaire, d'un aminosilaneuréido modifié et d'un vinylsilane organofonctionnel, et (c) un lubrifiant cationique, où l'ensimage formateur contribue à la dispersion des fibres de verre dans la dispersion aqueuse, les fibres de verre étant utilisées en une proportion telle qu'elles constituent de 1 à 50% en poids de la nappe ou bande déposée à l'état humide à former;

(B) on élimine l'eau de la dispersion aqueuse de l'étape (A) pour former un mat analogue à une feuille, déposé à l'état humide, et

(C) on applique au mat analogue à une feuille, déposé à l'état humide de l'étape (B), un liant pour le mat possédant une teneur en solides qui fluctue de 0,1 à 32% en poids et comprenant

(1) un polymère thermoplastique et chimiquement modifié, choisi parmi les polyoléfines à modification carboxylique;

(2) un polymère filmogène choisi dans le groupe constitué des polymères du type époxy, des polymères du type polyuréthane, des copolymères du type époxy-polyuréthane, de la polyvinylpyrrolidone et des polyoxyalkylènes;

le liant pour mat étant appliqué en une proportion telle que le polymère thermoplastique chimique modifié qu'il contient constitue de 0,01 à 20% en poids de la nappe ou bande déposée à l'état humide, et

(D) on sèche le mat analogue à une feuille, déposé à l'état humide, traité par le liant pour mat de l'étape (C) pour former une bande ou nappe déposée à l'état humide, non tissée, contenant des fibres.

2. Procédé suivant la revendication 1, caractérisé en ce que la dispersion aqueuse de l'étape (A) contient un ou plusieurs surfactifs afin de produire une dispersion aqueuse de mousse.

3. Procédé suivant la revendication 1 ou 2, caractérisé en ce que l'on incorpore au moins un antioxydant.

4. Procédé suivant la revendication 3, caractérisé en ce que l'antioxydant est choisi dans le groupe formé par les antioxydants du type thioester, les antioxydants du type phosphite, les antioxydants du type amine aromatique et leurs combinaisons.

5. Procédé suivant l'une quelconque des revendications 1 à 4, caractérisé en ce que le polymère formant la matrice thermoplastique est du polypropylène.

6. Procédé suivant l'une quelconque des revendications 1 à 5, caractérisé en ce que le copolymère ou le polymère filmogène soluble dans l'eau (a) contenu dans l'ensimage formateur dont les fibres de verre sont pourvues, possède une viscosité intrinsèque inférieure à 150 centipoises, un poids moléculaire variant de 22 000 à plus de 105 000 et est un polymère du groupe constitué par (i) le poly(acétate de vinyle) hydrolysé jusqu'à au moins un degré suffisant pour être soluble dans l'eau, (ii) la poly(vinylpyrrolidone), (iii) la poly(hydroxyalkylcellulose), et (iv) des copolymères de monomères pour préparer les polymères (i) et (ii), le polymère étant présent en une proportion allant jusqu'à 98% en poids des solides de l'ensimage formateur.

7. Procédé suivant l'une quelconque des revendications 1 à 6, caractérisé en ce que l'alcoxysilane organofonctionnel, essentiellement dépourvu de fonctionnalité du type monoamine primaire, qui est une espèce d'agent de couplage organique (b) contenu dans l'ensimage formateur de fibres de verre, est un uréidotrioxysilane organofonctionnel, hydrolysé, partiellement hydrolysé, ou non hydrolysé, où ledit trioxysilane sous toutes ses formes est présent en une proportion qui varie de 0,4 à 20% en poids des solides de l'ensimage formateur.

8. Procédé suivant l'une quelconque des revendications 1 à 6, caractérisé en ce que l'alcoxysilane organofonctionnel essentiellement dépourvu de fonctionnalité du type monoamine primaire, qui est une espèce de l'agent de couplage organique (b) contenu dans l'ensimage formateur de fibres de verre, est un vinyltrialcoxysilane organofonctionnel, hydrolysé, partiellement hydrolysé, ou non hydrolysé, où ledit trioxysilane sous toutes ses formes est présent en une proportion de 0,4 à 20% en poids de l'ensimage formateur.

9. Procédé suivant l'une quelconque des revendications 1 à 8, caractérisé en ce que le lubrifiant cationique (c) con-

tenu dans l'ensimage formateur de fibres de verre est présent en une proportion qui varie de 0,1 à 15% en poids de l'ensimage formateur.

- 5 10. Procédé suivant l'une quelconque des revendications 1 à 9, caractérisé en ce que l'ensimage formateur des fibres de verre est présent en une proportion qui varie de 0,15 à 0,45% en poids des fibres de verre.
- 10 11. Procédé suivant l'une quelconque des revendications 1 à 10, caractérisé en ce que le liant pour mat appliqué à l'étape (C) comprend un polymère thermoplastique chimiquement modifié (1) qui est neutralisé ou pratiquement neutralisé avec une base organique ou inorganique.
- 15 12. Procédé suivant l'une quelconque des revendications 1 à 11, caractérisé en ce que le liant pour mat appliqué au cours de l'étape (C) comprend le polymère thermoplastique chimiquement modifié (1) du liant pour mat sous forme d'une émulsion ou d'une dispersion aqueuse.
- 20 13. Procédé suivant l'une quelconque des revendications 1 à 12, caractérisé en ce que le liant pour mat appliqué au cours de l'étape (C) comprend un polymère thermoplastique chimiquement modifié (1) choisi dans le groupe constitué par le polypropylène modifié à l'anhydride maléique, le polypropylène modifié à l'acide maléique et leurs mélanges ou combinaisons.
- 25 14. Procédé suivant l'une quelconque des revendications 1 à 13, caractérisé en ce que le liant pour mat appliqué au cours de l'étape (C) comprend, en outre, un ou plusieurs agents de couplage aminoorganiques comportant une amine primaire avec une alcalinité supérieure à celle de la diéthyléthanamine.
- 30 15. Procédé suivant la revendication 14, caractérisé en ce que l'agent de couplage aminoorganique est un silane aminoorganofonctionnel choisi dans le groupe formé par les aminoalkylalcoxysilanes et les polyaminoalkylalcoxysilanes.
- 35 16. Procédé suivant l'une quelconque des revendications 1 à 15, caractérisé en ce que le liant appliqué au cours de l'étape (C) comprend, en outre, un anhydride et/ou acide mono- ou polycarboxylique, aliphatique ou cyclique.
- 40 17. Procédé suivant l'une quelconque des revendications 1 à 16, caractérisé en ce que le liant pour mat appliqué au cours de l'étape (C) comprend, en outre, un agent stabilisateur choisi parmi les agents de désactivation des métaux, les antioxydants à basse température et les antioxydants à haute température.
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